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Electron Mobility in a Novel Hyper-branched Phthalocyanine Dendrimer**

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Novel copper phthalocyanine (CuPc) materials have potential applications in solar cells, fuel cells, optical-limiting materials, gas sensors and field-effect transistors.^[1–10] Most recently there have been interests in applications for high dielectric constant material for capacitors.^[11,12] For example, Zhang et al. have reported a dielectric constant of ~ 48 at 1 MHz in an electrostrictive polymeric CuPc/Polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE) composite.^[11] However, a relatively high dielectric loss (>0.4) exists in such system due to the percolation limit of the CuPc filler. More recently, we have observed a very high intrinsic dielectric constant, coupled with a small dielectric loss (<0.01 up to 1 MHz) in a newly developed hyper-branched CuPc dendrimer.^[12] Although numerous reports have demonstrated the dielectric performance of CuPc polymers, the understanding of the electronic and optical behavior in dendrimers is limited, which is essential in the development of new materials. In this communication, the charge carrier mobility of a newly developed CuPc dendrimer is investigated. The synthesis of the CuPc dendrimer has been previously reported and is shown in Scheme 1.^[12] This hyper-branched CuPc has dendritic-like structure consisting of four –CN groups incorporating into the CuPc core. Moreover, our previous experience in the study of triarylamine-based dendrimers and ladder oligomers using the ultra-fast spectroscopy suggested a coherent energy migration process occurred and polaron delocalization states are possible.^[13] Time-resolved spectroscopy measurement has been carried out to study the optical behavior of this dendrimer. Our investigation has suggested the formation of delocalized polarons in the system. The super-conjugation effect from the oxygen atom and an increase of system packing through the self-assembling of phthalocyanine rings give polaron hopping and polaron tunneling between phthalocyanine rings.

In order to probe the electronic properties of this dendrimer, we carried out time-of-flight measurements to investigate the electron mobility. CuPc dendrimer was first dissolved in *N,N*-dimethylacetamide (DMAc) solution at a concentration of 1 mg mL^{-1} , then the CuPc/DMAc solution was drop-cast on a silicon wafer with a thickness of $500 \text{ }\mu\text{m}$. After drying in a

vacuum oven at $120 \text{ }^\circ\text{C}$ for several hours, a dendrimer film with a thickness ranging between 4 to $5 \text{ }\mu\text{m}$ was obtained using a surface profiler. Further details of the procedure are in the experiment section.

A typical transient current at an applied field of 5 V at several different temperatures is depicted in Figure 1 plotted on a linear scale. The transient current signals at room temperature follow a plateau region after a fast decay, then slowly tail off. This shows the characteristics of non-dispersive charge carrier transport. However, upon lowering the temperature, an apparent transition from non-dispersive to dispersive charge carrier transport occurs, which indicates that the disorder increases as temperature increases in this dendrimer system and agrees well with the disorder formalism predication by Bässler and co-workers.^[14] The dispersive charge transport may originate from the hopping between localized states. This agrees with the observation in the ultrafast depolarization and fluorescence dynamics (see below).

For these typical transient curves, the mobility can be calculated by Equation 1.

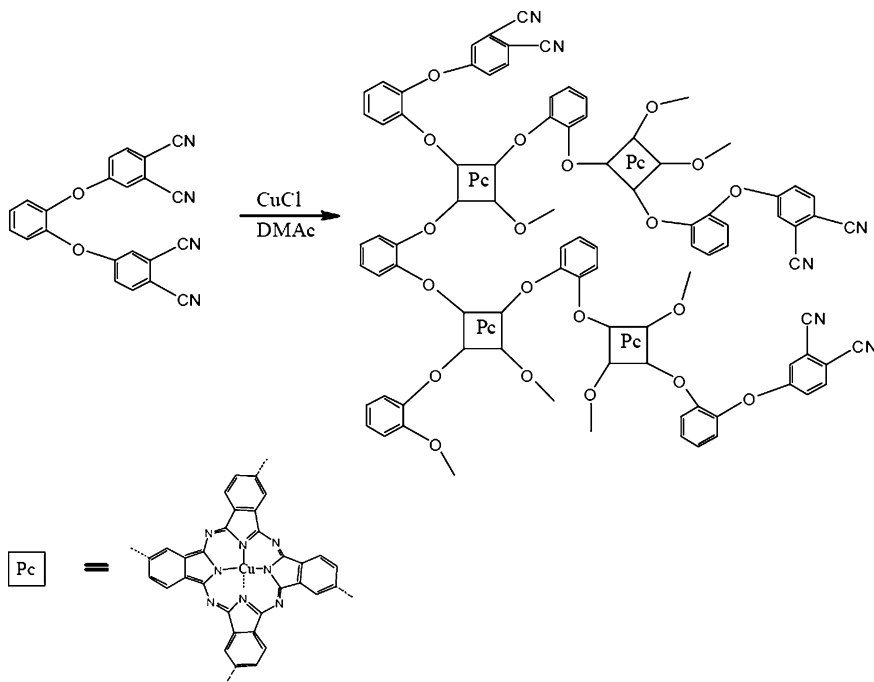
$$\mu = \frac{d^2}{t_{tr} \cdot V} \quad (1)$$

In Equation 1, μ is the mobility, d is the thickness of the film, t_{tr} is the charge carrier transit time and V is the applied electric field. A significant charge carrier mobility in the order of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ can be obtained, which is within the same order compared to the value observed for CuPc crystalline film by Micielski W. et al.^[15] The investigation of CuPc morphology by using TEM showed aggregates formed by large spherical crystalline domains of $\sim 60 \text{ nm}$, which may help to rationalize the high charge carrier mobility in this hyper-branched system. The fast displacement of charge carriers and large carrier mobility also support the high dielectric response observed at high frequency in this dendrimer system.^[12]

As supported by previous experimental results of the charge transport in disordered organics, the mobilities are usually low (with a magnitude between $10^{-7} \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ and $10^{-10} \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$) and strongly temperature and electric-field dependent in the case of a hopping dominated charge transport.^[16–20] And generally, the transport of charge carriers in polymers are slower than that in crystalline solids.^[20] However, the electron mobility in this novel dendrimer system is actually high. Thus we looked into the temperature and electric-field dependence. In Figure 2, the temperature dependence of the mobility is

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Scheme 1. The structure of Hyper-branched CuPc dendrimer.

illustrated. The measurements have been carried out at an electric field of 5 V. Generally, at high temperatures, thermal excitation of the carriers to the band edges is possible for a Pc semiconductor and extended-state conductivity can occur. At low temperature less thermal energy is available and polaron hopping may dominate.^[14] Thus, a high mobility at higher temperature is typically observed in contrast to this negative temperature dependence observed in this dendrimer system. This non-Arrhenius behavior may be suggested to originate from positional dielectric disorder.^[21] When the temperature is decreased, due to the self-organization of the CuPc planar structures, a tighter stacking of the CuPc rings may become possible, which may shorten the hopping distance of the polaron between the CuPc rings in the system. Also, when the

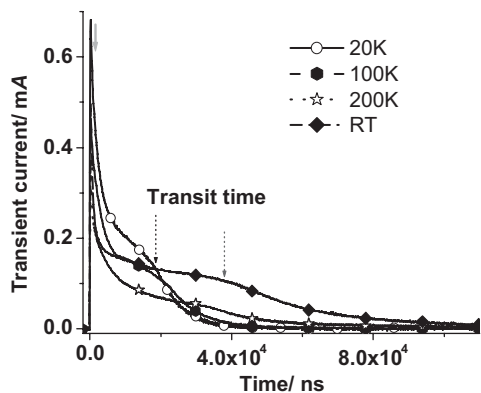


Figure 1. The transient current of the CuPc dendrimer/Silicon film with an applied voltage of 5 V at various temperatures. * The sharp peak indicating electron transportation in silicon wafer.

distance between CuPc rings becomes short enough ($<5 \text{ \AA}$), polaron tunneling may occur at a very low temperature.^[22]

This also provides support that a super-linear power law relationship of AC conductance (given by expression $\sigma_{AC} = A + B \omega^s$ where A and B are constants related to the zero frequency conductivity and s is a fitting parameter) is obtained here by yielding an s value of 1.7, as shown in Figure 3. Vidadi et al. has suggested a charge transport mechanism dominated by polaron hopping and band-type mechanisms in CuPc film with an s value of 1.75.^[23]

If the temperature dependence is replotted in an Arrhenius format, as illustrated in the inset of Figure 2, as the temperature decreases, the mobility increases and obeys the $\mu \propto 1/T$ relation, a characteristic of non-Arrhenius behavior, but it tends to saturate at lower temperatures, such as a dispersive transport regime. There is a weak temperature dependence of the mobility, because

when the temperature decreased from 200 K to 20 K, only a three-fold increase was observed. Extrapolating to the limit $1/T \rightarrow 0$ based on the fitting, μ_0 with a value of $2.27 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ is found with 5 V applied field. The weak temperature dependence may indicate that the polaron tunneling becomes more dominant at low temperature, because less hopping sites will be available once the system disorder is reduced at lower temperature.

Furthermore, if we look at the activation energies derived from the fitting of data in Figure 2 inset at two different applied field, we can find that the activation energy decreases at low electric field (with a value of 0.0106 eV at 5 V applied field and a value of 0.0168 eV at 12 V applied field, respectively). This decrease in activation energy indicates more hopping sites will be

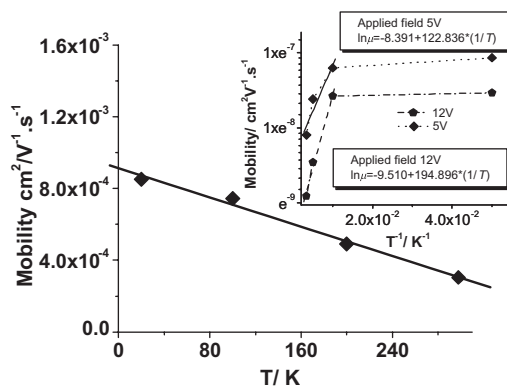


Figure 2. The temperature dependence of charge carrier mobility at an applied voltage of 5 V. The inset is the Arrhenius plot of the charge carrier mobility at two different applied electric field, 5 V and 12 V, respectively.

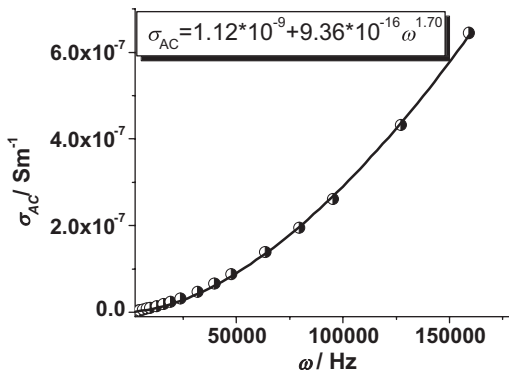


Figure 3. AC conductance of the CuPc dendrimer pellet.

available at low electric field, therefore a high mobility should be expected at low electric field. The low activation energy may also suggest that the polaron formation contribution should be considered in combination with energetic and positional disorder suggested by Bässler and co-workers,^[14] because polaron has a strong effect on the low temperature activation energy relaxation in disordered organic materials.^[24]

Shown in Figure 4 is the applied field strength dependence of the charge mobility in the dendrimer film with a thickness of $\sim 4\mu\text{m}$. It is apparent that the mobility dependence on the electric field follows a relation of $\mu \propto E^{1/2}$, a typical Poole–Frenkel-like behavior.^[25] The slope of the electric field dependence decreases with the increasing of temperature (from 20 K to RT, the slope drops from -1.41578 to -1.7867), which indicates that the mobility becomes a less strongly positive function of field and satisfies the prediction from disorder formalism.^[14] As the typical Poole–Frenkel dependence of the mobility on the electric field has no correlation with the electrode type, thus may be associated with the charge carriers and the positional disorder of hopping sites, which has been found in other organic materials, such as polythiophenes.^[25,26] In contrast to the observed field dependence characteristic in the phthalocyanine monomer film, a negative dependence occurs, which has been found in various disordered organic materials.^[25–29] In addition, numerous

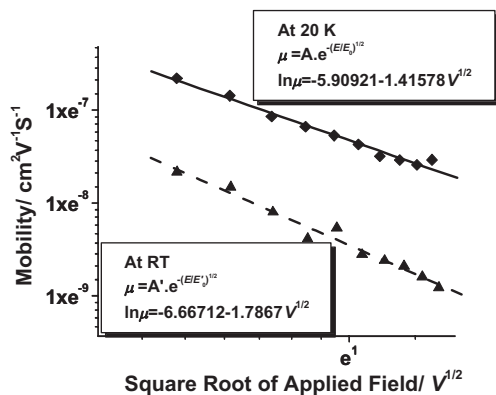


Figure 4. Charge carrier mobility versus square of electric field strength at different temperatures.

Monte Carlo simulations of charge transport have reproduced such effect based on a Gaussian disorder model (GDM).^[14,28] Currently, there are several major arguments surrounding this negative field dependence.^[25,29–30] One argument states that the negative dependence occurs due to the limitation of TOF technique, for example, the dielectric relaxation time is longer than the injected carrier transit time, a prerequisite for TOF application is no longer satisfied.^[30] However, this explanation contradicts to some experimental results. Herein, Cordes et al. draw the conclusion that this effect can be attributed to the predominance of diffusion at low field.^[29] Another explanation was given by H. Bässler and his co-workers.^[25] They found that this effect is an inherent property of the hopping transport in disordered solids by extending the disorder model within the framework of an effective medium approach (EMA), in addition to the consideration of polaron formation contribution. We infer that the hyperelectronic polarization diminishes in a weak field and there is a larger degree of positional disorder at high electric field in this dendrimer system.

The TOF signals of the novel CuPc dendrimer show characteristics of Gaussian transport, as described by Bassler’s uncorrelated Gaussian disorder model (UGDM). In this model, the zero field mobility $\mu(0, T)$ and the field activation of the mobility $\gamma(0, T)$ have $1/T^2$ temperature dependence and can be expressed as:

$$\mu(0, T) = \mu_0 \times \exp(-2/3(\sigma/k_B T)^2) \quad (2)$$

$$\gamma(0, T) = C((\sigma/k_B T)^2 - \Sigma^2) \quad (3)$$

Where σ is the width of the Gaussian distribution of hopping sites, C and Σ are the parameters of the model. From the fitting, we obtained a value of $2.627 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for μ_0 , which is comparable to that for CuPc with a value of $2.8 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[31] In addition, a relatively weak energetic disorder in this organic system was found. Also, earlier reports of simulations of charge transport also supported the fact that the negative electric field dependence occurs at strong positional disorder and weak energetic disorder in a disordered organic solid system.^[25] As the positional disorder increases at lower field, faster paths are opening and charge transport occurs within a percolation type cluster of hopping sites with a relatively small hopping distance, which results in a larger probability of charge hopping. The negative electric field dependence in combination with non-Arrhenius temperature dependence is in agreement with the AC conductance analysis of this dendrimer system.

In order to have a better understanding of the charge transport mechanisms in this novel dendrimer system, we also carried out steady-state absorption and emission spectroscopy. Figure 5 shows the absorption and emission spectra of CuPc solution. Four main UV-Vis absorption bands are observed. The strong absorption peaks are dominated by Soret bands, Q and B band. The absorption at 336 nm is assigned to B band ($\pi-\pi^*$ transitions of the macrocycle). Precedent to B band

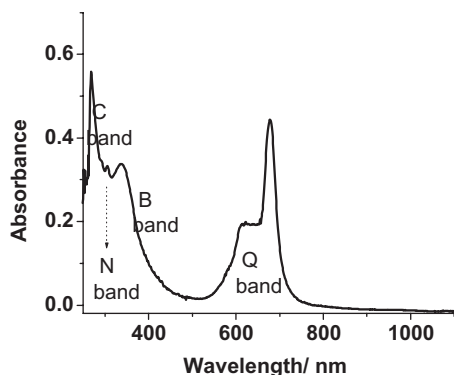


Figure 5. Absorption spectra of CuPc dendrimer.

peak, other two absorption peaks in UV range may be assigned to N (305 nm, $d-\pi$) and C (259 nm, $d-\pi^*$) bands, respectively. A strong Q-band absorption peak is observed at 678 nm and attributed to the $\pi-\pi^*$ transition on the phthalocyanine macrocycle, similar to published spectroscopic features of CuPc rings.^[32–34] Accompanying the Q-band, there is a relatively weak peak, seen as a shoulder, appears at 624 nm may be assigned to metal-to-ligand charge transfer.^[34]

When excited at 624 nm, a weak emission peak was observed which confirms our assignment of metal-to-ligand charge transfer to the band at 624 nm in this dendrimer. Moreover, no emission is observed at an excitation in higher energy bands. For example, when excited at B band or at 400 nm, no emission is observed by the steady state measurement. It's interesting to note that the emission spectrum at 624 nm is not exhibiting mirror symmetry to the adsorption spectrum. This distortion may indicate a symmetry breaking after the excitation, which agreed to the observation of femtosecond fluorescence dynamics illustrated in Figure 6. The results show that the fluorescence decay of this dendrimer possesses two components, including a fast component on a time scale of 120 fs, which was within the range of the IRF. Initially, the fluorescence decays fast with an anisotropy residue of 0.2,

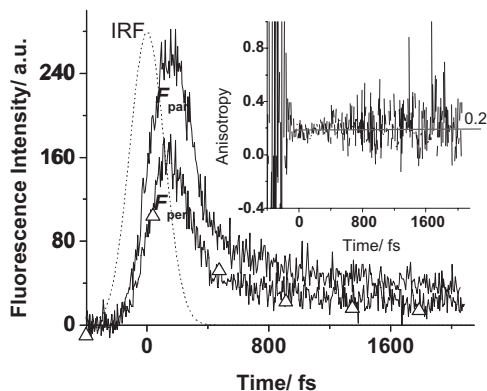


Figure 6. B-band fluorescence dynamics and fluorescence decay (inset) of CuPc dendrimer at an excitation of 400 nm.

which indicated the symmetry breaking in the delocalized system and the excitation was transferred to other rings. Otherwise, we should expect a residue value of 0.1 in this planar structure, with the exciton located on one ring. In addition, it provides evidence to the electron hopping process suggested in this dendrimer system, because the breaking in symmetry could possibly induce more traps to form. The slow component was on a time scale of 3 ps, comparable to many exciton hopping processes observed and which may be attributed to electron hopping process between neighboring CuPc rings in the excited states. All above characteristics shown in CuPc dendrimer spectra indicate non-radiated relaxation pathways, for instance, ring-to-ring charge transfer or ring-to-metal charge transfer process involved.^[13,35]

In summary, we have observed non-Arrhenius and Poole-Frenkel behavior in this dendrimer system. The non-dispersive to dispersive transformation occurred when the temperature decreased, due to the self-organization of CuPc rings, creating more polaron hopping, as well as polaron tunneling pathways. The time-of-flight measurements demonstrated a fast movement of the carriers in the system (under sub microsecond with a low drain voltage) and the significant carrier mobility ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), may provide strong evidence to the strong and fast dielectric response in this dendrimer system. The impressive dielectric response in this dendrimer system can be attributed to polaron hopping and tunneling charge transport mechanisms.

Experimental

Steady-State Absorption and Emission: UV-visible absorption spectra were recorded with an Agilent Technologies 8453 spectrophotometer, and the fluorescence spectra were measured with a Shimadzu RF-1501 spectrofluorophotometer.

Time-of-Flight Mobility Measurement: The CuPc dendrimer/DMAC solution was cast onto silicon wafer ($\sim 500 \mu\text{m}$). Then it was sandwiched between gold electrodes using vacuum deposition. A 337 nm N_2 laser pulse of 10 ns duration was used to excite the transient current. An electric field was applied across the sample by applying a potential difference between the electrodes.

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